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Synthesis of New Complexes by Using Pyridine Acetohydrazone Derivatives

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Abstract
A new ligand L_1=[N-(1-pyridine-2-yl)Ethlidene AcitoHydrazide]; was synthesized by condensation of acetohydrazide with Acitil pyridine. Then the complexes were synthesized by reacting the transition metals (Co^{2+},Cr^{3+} , Fe^{2+}) with the ligand [with a metal to ligand ratio of (1:2) respectively] and this led to forming the following complexes : $[Co(L_1)_2]$ Cl_2 , $[Cd(L_1)Cl]$, $[Fe(L_2)SO_4]$ .The ligands and complexes were characterized and studied on the basis of FT-IR, and U.V.–visible and the results were compatible with the proposed structures
Keywords: ligand, metal complexes, pyridine.

1. Introduction

Schiff bases are those compounds containing the active isomethyne group R_1R_2C = N -, which is due to multiple electronic and Stereotypical properties. The complexes formed by Schiff's bases with transitional metals ions were widely studied [1,2] and the spacial structure of a number of them was determined. The bases of Schiff with their properties are very useful compounds in the field of analysis and chemical separation. They are Clutch compounds used in copper calibration selectively [3]. They were also used as extraction factors for the determination of bi- copper as a photic[4] and chromatography to determine nickel in some natural food samples [5] . They were also used in the micro accurate determination of bi- cobalt photic[6] , as well as in the process of extracting the ionic pair of binary metal cations [7] . The bases of Schiff derived from ketone condensation with the primary amines were named Ketimines [8]. The compounds derived from aldehydes condensation with amines were called Aldimines [9]. And in the case of condensation of hydrazidates with ketones or aldehydes in suitable Solvents, condensation products are called hydrazones [10] .

2. Experimental

2.1 Materials

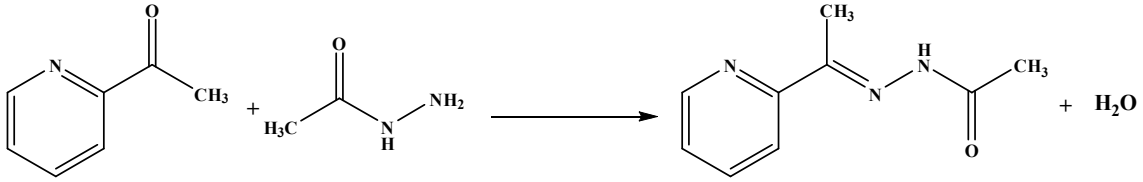
All the chemicals used were purchased from both Merck and Sigma Aldrich companies and used without further purification. FT-IR spectra was recorded using Jascow Japanese taype (A) Infrared Spectrophotometer Fourier Transform FT-IR-4100 (KBr). UV spectra was measured on Optizen spectrophotometer 200 -800nm.

3. Results and Discussion

3.1 Synthesis of a Schiff base ligand

The Schiff base ligand used in this study was prepared by refluxing an equimolar mixture of acitel pyridine and the respective hydrazide in methanolic medium. A typical synthesis is described below.

30 ml methanol solution with acitel pyridine (1.136 g, 10 mmol), acito hydrazide (0.74g, 10mmole) with 50 ml methanol were added and the reaction mixture was stirred while refluxing for 3 h. Then the volume of the resultant was reduced to ≈30 ml. The solid resultant was filtered and thoroughly washed with ethanol (2 × 5 ml) followed by diethyl ether (2 × 5 ml). The solid was recrystallized by hot ethanol, Scheme 1.



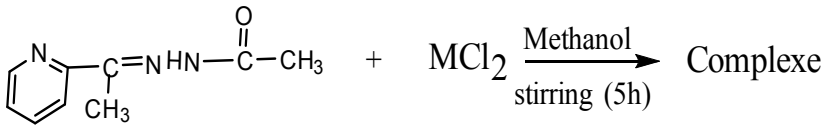
Scheme 1. Synthesis route of the main reaction.

3.2 Syntheses of the complexes

All the complexes were prepared following a similar method of reacting a methanol solution with the metal salt[with a metal to ligand ratio of (1:2) respectively]. Preparation of one of the complexes is described below .

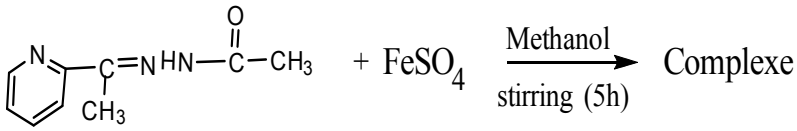
To a 50 ml methanol solution , the ligand (1 mmol), was added with stirring. When the dissolution is completed. Addition of MCl2 anhydrous (0.5 mmol) when [M =Co^{2+},Cr^{3+}] and [$FeSO_4$] anhydrous (0.5 mmol) in case of using (Fe^{2+}) to the colorless solution produced colored solution immediately. After 5 h of stirring the volume of the solution was reduced to ≈20 ml and filtered. The solid resultant was obtained and washed with

methanol (3 × 3 ml), followed by diethyl ether (2 × 5 ml), Scheme 2. Results of the compositional and spectroscopic analyses are shown in Tables 1-5.



$M=Co^{II},Cr^{III}$

Scheme 2. The main Synthesis of complexes.



Scheme 3. Reaction between the ligand and sulfate iron (II).

Table 1: Characterization of the Schiff base Ligands and metal(II) Complexes.

Compounds	Formulas	Color	m.p°C	Yield (%)
L	$C_9H_{11}N_2O_1$	White	160	50
$[Co(L)_2]Cl_2$	$C_{18}H_{22}N_4O_2CoCl_2$	green	250-dec	40
$[Cr\ (L)_2\ ]Cl$	$C_{18}H_{22}N_4O_2CrCl$	green	210-dec	38
$[Fe(L)_2SO_4]$	$C_{18}H_{22}N_4O_6FeS$	black	280-dec	60

3.3 FT-IR spectra of the (L) ligand and its complexes*:*

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} helps to indicate regions of absorption vibrations. The main stretching modes are for ν(C=N), ν(C=C) and ν(C=O). The IR data of the spectra of Schiff base ligand (L) and its complexes are presented in Table 3. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation.

Spectrum of the (L) ligand shows a sharp band at (1677cm^{-1}) due to ν(C=N) azomethine group which has shifted to lower frequency about (70cm^{-1}) in the complexes indicating its participation in chelation through azomethine nitrogen. The lowering of band is due to the reduction of electron density in the azomethine link. Pyridine ν(C-N) shows absorption band at (1298cm^{-1}) in the Schiff base spectrum. This band makes shift by (1271cm-1) in the complex. Azomethine group in the Schiff base (L) changed after complication .with Co(II) from (1677cm^{-1}) to (1638cm^{-1}) this indicate that involvement of Azomethine group in complications.

Table 2. Characteristic infrared absorption frequencies (cm^{-1}) of the ligand and complexes.

compounds	ν(NH)	ν(C=N)	ν(C=N) $(C=N)_{Py}$	ν(C=O)	ν(C-H)SP^2
L	3192_t	1617_{st}	1577_m	1677_m	2924_W
$[Co(L)_2]Cl_2$	3187_{st}	1518_{st}	1463_m	1638_m	2922_W
$[Cr\ (L)_2\ ]Cl$	3213_{st}	1602_{st}	1557_m	1673_m	2925_W
$[Fe(L)_2SO_4]$	3199_{st}	1638_{st}	1601_m	1654m	2965_W

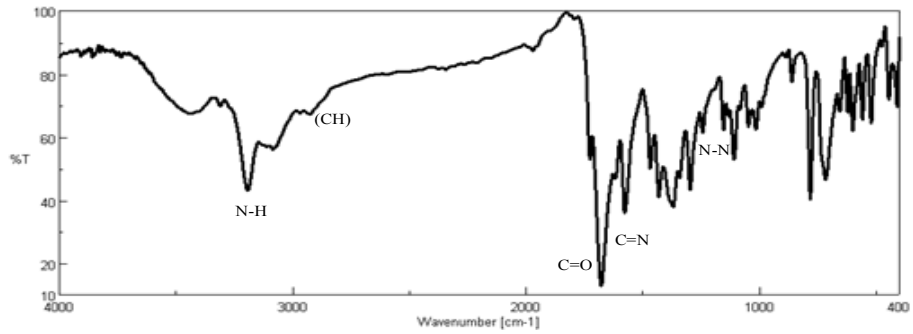


Figure 1:FT-IR spectrum of ligand (L)

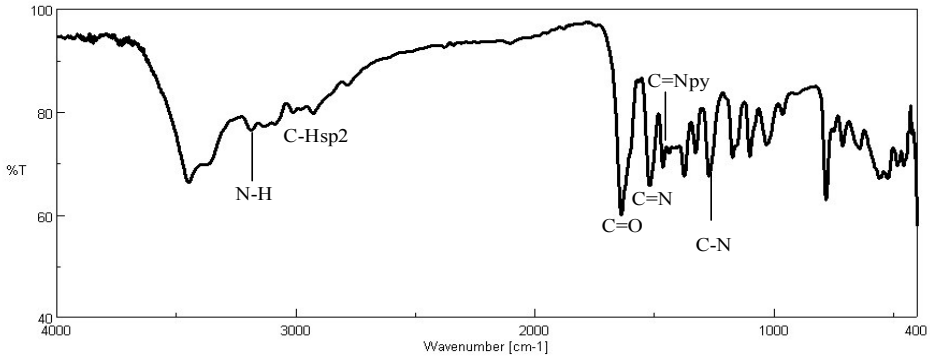


Figure 2:FT-IR spectrum of complex $[Co(L)_2]Cl_2$

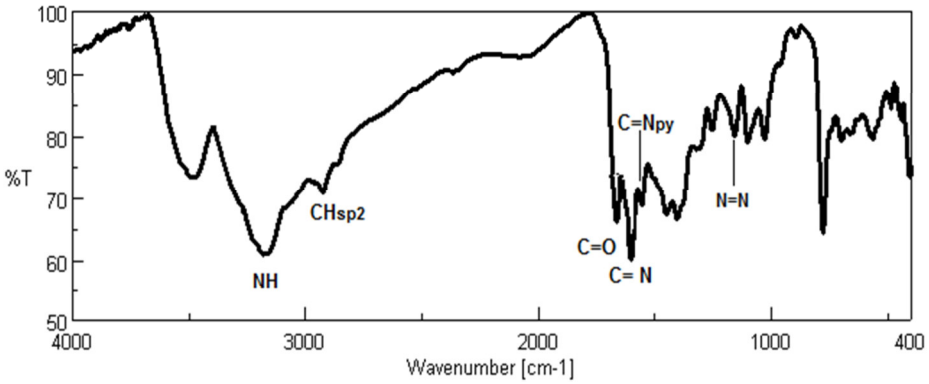


Figure 3:FT-IR spectrum of complex $[Cr(L)_2]Cl$

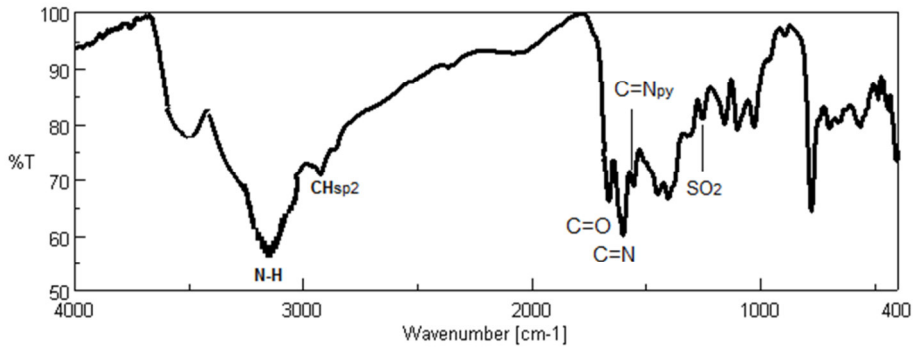


Figure 4: FT-IR spectrum of complex $[Fe(L)_2SO_4$

3.4 Electronic spectral data:

The data of the electronic spectra of the ligand and its complexes are given in Table 3. The spectrum of Schiff base (L) presented two bands in the UV interval at 210nm and 286nm , assigned to ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi^*$) transitions respectively.

The electronic spectra of the complexes in methanol solution has two bands at (270, 370)nm These bands may be assigned to the charge transitions (LMTC)of the form

($n \longrightarrow \pi^*$) for azomethine group (C=N) and the pyridine ring was assigned to metal ion $L \longrightarrow M$ [15] .

The position of these bands suggests an octahedral environment to Co(II),Cr(II) and Fe(II) .

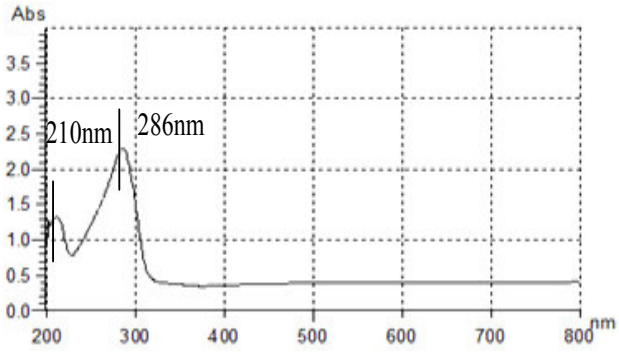


Figure 5: UV absorption spectrum of ligand (L)

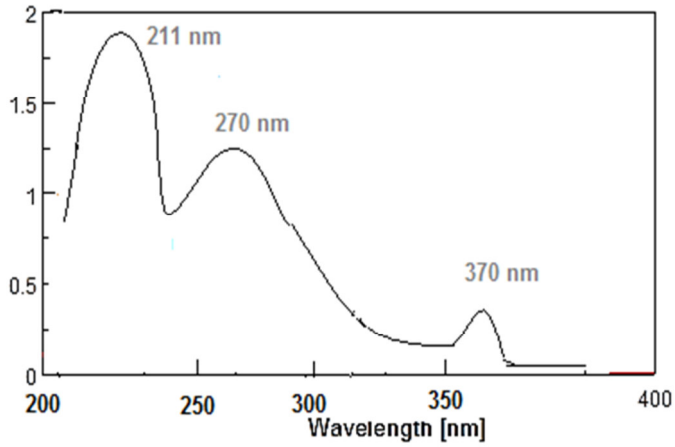


Figure 6: UV absorption spectrum of $[Co(L)_2]Cl_2$

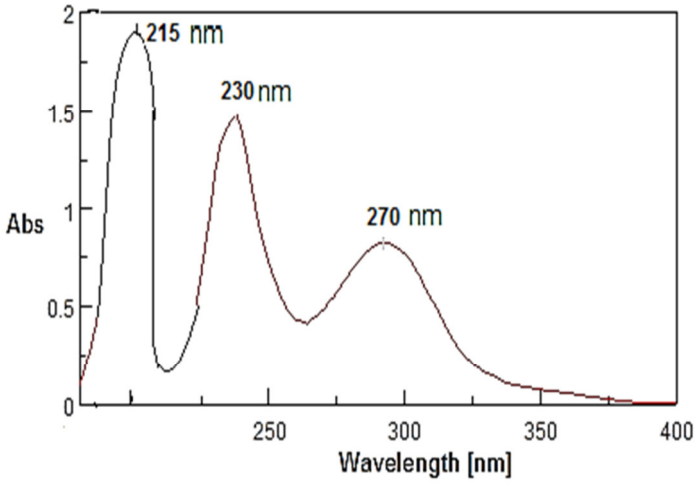


Figure 7: UV absorption spectrum of $[Cr\ (L)_2\ ]Cl$

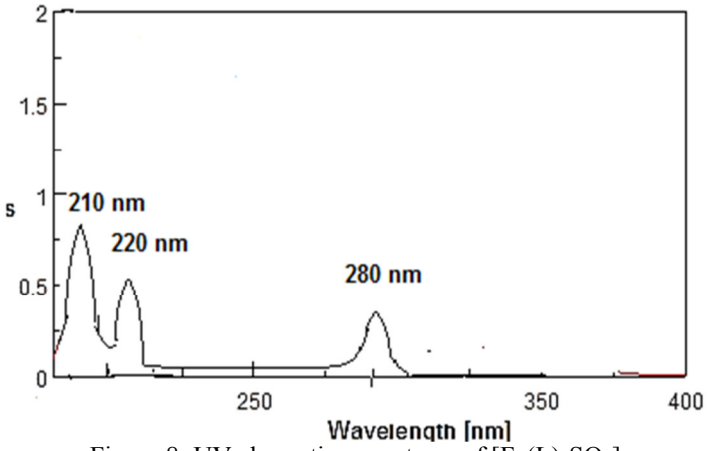


Figure 8: UV absorption spectrum of $[Fe(L)_2SO_4]$

Table3: Magnetic moments, electronic bands and ligand filed parameters of Land its metal complexes [11].

compound	π→π* (nm)	n→π* (nm)	L→M (nm)	d-d (nm)
L	210	286	---	---
$[Co(L)_2]Cl_2$	211	270	370	---
[Cr (L)2]Cl	215	230	290	---
$[Fe(L)_2SO_4]$	210	220	280	---

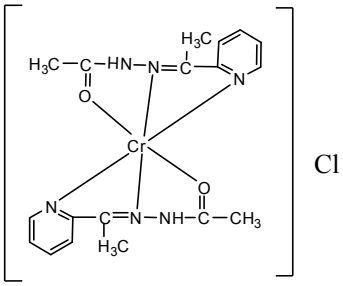


Figure 9: Suggested structures for the L complex with Cr^{III}

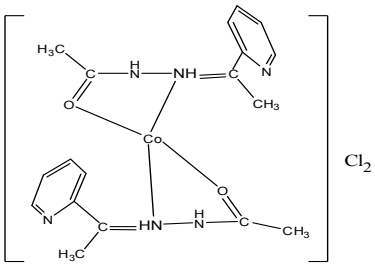


Figure 10: Suggested structures for the L complex with Co^{II}

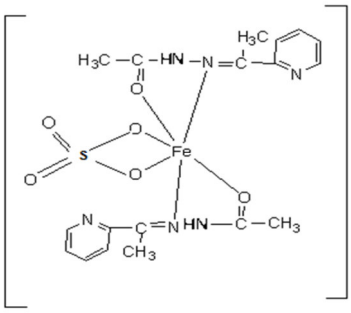


Figure 11: Suggested structures for the L complex with Fe^{II}

4. Conclusion

A new ligand L_1=[N-(1-pyridine-2-yl) Ethlidene AcitoHydrazide]; was synthesized by condensation of acetohydrazide with Acitil pyridine. Then the complexes were synthesized by reacting the transition metals (Co^{2+}, Cr^{3+}, Fe^{2+}) with the ligand [with a metal to ligand ratio of (1:2) respectively] and this led to forming the following complexes: $[Co(L_1)_2]$ Cl_2 , $[Cd(L_1)Cl]$, $[Fe(L_2)SO_4]$ .The ligands and complexes were characterized and studied on the basis of FT-IR, and U.V.–visible and the results were compatible with the proposed structures

5. Acknowledgment

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6. References

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